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first metal component which is within the interior pore structure of the molecular sieve and which comprises vanadium in an oxidation state greater than zero and (ii) a second metal component which is within the interior pore structure of the molecular sieve and which comprises at least one rare earth in a matrix comprising alumina or silica-alumina with clay.

~~Cancel~~ claims 13 to 25.

Remarks

1.1. This amendment is in response to the Official Action of 22 May 2001 (Paper No. 16). Entry of the amendments set out above is requested. A marked up copy of the amended claims is attached in accordance with the requirements of 37 CFR 1.121(b) and (c).

1.2. A copy of the following is enclosed with this response:

Fluid Catalytic Cracking Handbook, Sadeghbeigi, Gulf Publ., Houston, Tex., ISBN 0-88415-290-1, pages 79, 89-91.

Entry of this paper into the record under 37 CFR 1.132 is requested.

2.1. Accompanying this response is an Information Disclosure Statement, submitted under 37 CFR 1.97(c)(2) with the appropriate fee, which identifies two references which are relevant to the examination of this application. U.S. 4,794,095 and 4,846,960 (both to Walker, assigned to Philips). The Walker references disclose the use of cracking catalysts which are based on pure silica matrix materials in which the active zeolite cracking component, e.g. zeolite Y, is embedded (Walker '095, column 1, lines 37-38). In addition to the silica matrix and the zeolite, the catalyst contains at least one vanadium oxide (column 1, lines 42-45) in an amount which has been found to be effective for alleviating the problem of deactivation by the presence of vanadium in the cracking feeds (column 1, lines 17-22). The patent stresses the importance of using a pure silica matrix material for the catalyst: see column 8, lines 42-50.

2.2. By contrast, the claims of the present application claims are directed to the use of molecular sieves which contain vanadium as well as a rare earth component in matrices which are based on alumina or silica-alumina with added clay. Since the Walker references teach away from the use of matrices other than pure silica (see column 8, lines 42-50), it is believed - and it is so submitted - that the claims are patentable over the Walker references as well as those previously made of record. Further, the Walker references do not disclose the desirability of using the vanadium component in addition to the rare earth component with the objective of reducing liquid product sulfur content.

3.1. Applicants note the Examiner's position regarding the election/restriction requirement. To conserve effort in these proceedings, Applicants have canceled the claims directed to the catalytic compositions and will not press their position further at this point, save only to note that if the Examiner's arguments were to be accepted, it might lead to the conclusion (which seems quite open to challenge) that the requirements of the MPEP, a set of internal guidelines for the use of an administrative agency, supercede the requirements of the law (Section 706 of the APA), as established by the Congress and enunciated by the Supreme Court. See, for example, *SEC v. Chenery*, 318 US 80, 89 to 93 (1943). Although Applicants do not categorize the Examiner's example in this way (or even to make any such implication), it is pointed out that an example unsupported by credible factual evidence appears to be no more than argument since the most fanciful example could be conceived and advanced without reference to credible fact or accepted theory. For this reason, the requirements of the act, passed by a benevolent and far-seeing Congress, and as interpreted by a wise and omniscient Supreme Court, should have prevailed.

4. The claims, especially independent claims 1 and 11, have been amended to specify that the metal component of the sulfur reduction catalyst comprises vanadium. This amendment resolves the rejection under 35 USC 112.

5.1 The Examiner has rejected claims 1-6 and 8 under 35 USC 103(a) as obvious over Beck U.S. 4,588,702 in view of Kugler U.S. 4,944,864.

5.2. Applicant's position with respect to the Beck and Kugler disclosures was set out in some detail in the previous response, Sections 4 and 5. As the Examiner noted in

Paper No. 16 (page 5, top), Beck does not disclose the use of a catalyst containing vanadium. Attempting to remedy this deficiency for the purposes of the rejection, reference is made to Kugler, the Examiner stating that vanadium contaminants in cracking feeds remain on the catalyst during regeneration, are oxidized and become mobile to react with the zeolite components of the catalyst so that, as a result, the regenerated catalyst contains vanadium.

5.3. Assuming for the moment, the correctness of the Examiner's explanation, it is pointed out that this still does not a rejection make - at least, one that is proper. Even if Kugler is taken as a basis for the proposition that vanadium from cracking feeds reacts with the zeolite component of the cracking catalyst, Applicants do not concede that this satisfies the requirements of the present claims that the vanadium is present in the interior pore structure of the molecular sieve in an oxidation state greater than zero. Kugler, either alone or read in the light of Beck, does not disclose this feature, far less suggest its desirability. There is therefore nothing in the combined Beck and Kugler teachings which as a matter of words points towards the present invention. This point was discussed extensively in Section 5 of the previous response. Nor would such a result have been inherent in any operation of the Beck or Kugler processes.

5.4. The vanadium which is present in hydrocarbon cracking feeds such as gas oils is typically present, as noted by Kugler (column 1, lines 37-58) in the form of porphyrins which are condensed ring structure complexes. A speculation advanced by Kugler is that the vanadium from the feed migrates through the catalyst particle to accumulate in areas of high zeolite concentration (column 1, lines 54-58). This does not state or imply that the vanadium enters the pore structure of the zeolite in any particular form or even at all. All it does assert is that the vanadium migrates to areas of high zeolite concentration. Perfectly consistent with this statement is the proposition that the vanadium does not enter the zeolite but remains near but outside it and such a proposition would appear to be consistent with a consideration of the sizes of the various oxidized vanadium species relative to the pore sizes of the zeolites. Certainly, the Examiner has not cited any factual basis (e.g. pore sizes, sizes of oxidized vanadium species) to support any conclusion that the vanadium actually enters the interior pore structure of the zeolite. In fact, a close perusal of this rejection reveals not even an assertion that this would be so: the most that the examiner has said is that "the

regenerated catalyst contains vanadium". True, but hardly relevant; the claims require more, that the zeolite component of the catalyst contain the vanadium within the interior pore structure of the zeolite in an oxidation state greater than zero.

5.5. The Examiner's conclusion that "accumulation in high zeolite areas is considered to encompass any portion of the zeolite, including the pores" (Office Action, page 15) assumes too much: there is nothing in the reference which would lead the skilled person to expect that the vanadium would enter the pore structure. The reference does not state this nor is there reason to imply, to expect or suppose that it might happen. The purported factual predicate, that in order for the vanadium to migrate, it must pass through the pores is misplaced: the Kugler catalyst materials, as is conventional, contain a matrix of a porous oxide such as alumina or silica alumina (column 3, line 62; column 4, line 40) which is of a larger pore size than the sieve component, specifically in order to permit the movement (migration) of large molecular size species through the catalyst particles. See, for example, Sadeghbeigi, page 91. The Examiner's stated position therefore appears to be at variance with the facts.

5.6. The statement that since the Kugler reference "does not limit what portion of the zeolite the vanadium migrates to, it is considered to encompass any accessible part of the zeolite, including the pores" (Office Action, page 15) is an interesting conflation of error and speculation. It is not seen how this or any reference may "limit" what happens in actuality: it may describe a limiting factor but whatever stated, the present proceedings are governed by the what is explicitly disclosed in the reference as a document. The fact that it does not "limit", then means that it *does not disclose* that the vanadium migrates into the pore structure of the zeolite. This, in turn, means that the Examiner is not justified in simply assuming without more that it does so. At the very least, some soundly based scientific reasoning supported by substantial evidence of record is required to substantiate the asserted "position". Without such substantiation, the Examiner's conclusion must be concluded to be without support in any substantial evidence, as required by Section 706 of the Administrative Procedure Act. The rejection therefore lacks a sufficient factual basis to be proper. Reconsideration of this rejection is therefore in order.

6.1. Claim 7 has been rejected under 35 USC 103(a) as unpatentable over Beck in view of Kugler and Cooper, U.S. 5,601,798, newly cited. The Examiner has noted that several differences are noted between the reference of Beck and the claimed invention, including the specific UCS, the silica:alumina ratio of the USY composition as well as the use of the vanadium component (Paper No. 16, pages 5, 6).

6.2. The Cooper reference has been cited to show that it is conventional in the FCC art to crack a feed in the presence of a USY containing catalyst, with a rare earth component and a UCS in the range of 24.5 to 24.6Å (2.45-2.46 nm) and a silica:alumina ratio of 5-12. While the factual teachings of this reference with respect to zeolite USY are conceded, as they must be, the combination of references cited against claim 7 does not indicate the obviousness of using vanadium in the catalyst with this component located within the interior pore structure of the sieve in any particular oxidation state. As pointed out in Section 5 above, there is no factual predicate for believing that vanadium from cracking feeds enters the interior pore structure of the sieve component of the catalyst far less any suggestion or implication that it would have been expected to have any desirable effect on the sulfur content of the liquid cracking products. Given also the strong prejudice in the art against the presence of vanadium in the presence of zeolite cracking catalysts (see Wormsbecker, of record) it would not have been obvious to one of ordinary skill in the art to use vanadium in an FCC catalyst at all. The skilled person would have been motivated not only by the absence of any expectation of utility but also by because of its undesirable effects both upon the catalyst as a whole (see Beck) and specifically, the sieve (zeolite) component of the catalyst (see Kugler). Applicant therefore rejects the suggestion that it would have been obvious to utilize a vanadium containing catalyst because of Kugler's teaching regarding the presence of vanadium components in the FCC process. Reconsideration and withdrawal of the rejection of claim 7 is therefore required.

7.1. Claims 9-12 have been rejected under 35 USC 103(a) as unpatentable over Beck in view of Occelli, U.S. 4,615,996. The Occelli reference is relied on to support the proposition that is conventional in the art to use FCC catalysts with particle sizes less than 75 microns. This much was previously conceded although it was pointed out that the specific passages cited by the Examiner did not appear to support the

proposition. A more relevant portion of the Occelli reference would be the passage at column 7, lines 59-67.

7.2. With respect to the substantive merits of this rejection, the comments set out above with respect to the Beck and Kugler references are reiterated. There is nothing in Beck which indicates the desirability and therefore the obviousness of using a catalyst which contains vanadium within the interior pore structure of the molecular sieve in an oxidation state greater than zero in combination with rare earth within the interior pore structure of the sieve. Kugler does not, for the reasons previously given, supply this shortcoming. In addition, as noted above, the use of vanadium would have been considered highly undesirable in the art, especially when specifically combined with the zeolite component of the catalyst. This rejection should therefore be withdrawn.

8. The rejection based on the Balko and Schorfheide references was not applied to claim 4 which recited the use of vanadium as the first metal component in the sulfur reduction composition. With the amendment of the claims to specify that vanadium is present as this component, it is taken that this rejection is no longer applicable.

9. The prior art rejection based on Balko, Schorfheide and Cooper and is applied to claim 7. It does not appear to be justified because none of these references teaches the desirability of using vanadium in an oxidation state greater than zero in the interior pore structure of a molecular sieve component of a matrixed catalytic material in combination with a rare earth component in an alumina-containing matrix for the purpose of reducing the sulfur content of the liquid cracking products of a catalytic cracking process. In fact, none of these references appears even to disclose the use of a molecular sieve containing vanadium in the requisite oxidation state. Reconsideration of this rejection is therefore requested.

10. The final prior art rejection based on the Balko, Schorfheide and Kugler references was applied to claims 4 and 9 to 12. As discussed above, neither Balko nor Schorfheide discloses the use of vanadium as a component of a catalytic material and, for the reasons set out in Section 4 above, Kugler does not remedy this deficiency. The references do not, either alone or in combination, disclose or suggest the desirability of

using vanadium in an oxidation state greater than zero in the interior pore structure of a molecular sieve component of a matrixed catalytic material in combination with a rare earth component in an alumina-containing matrix for the purpose of reducing the sulfur content of the liquid cracking products of a catalytic cracking process. Reconsideration of this rejection is therefore requested.

11.1. The final rejections made by the Examiner are a series of double-patenting rejection based on the following co-pending applications:

Serial No. 09/221,540 (Mobil Case 10102-1)

Serial No. 09/468,452 (Mobil Case 10102-2)

Serial No. 09/144,607 (Mobil Case 10061-1)

These rejections are provisional in character since none of the predicate applications has issued as a patent. Applicant does not concede the correctness of these rejections. The reasons for militating against a conclusion of double patenting with respect to Serial No. 09/221,540 were set out in the previous response and apply with like force to Serial No. 09/468,452 which is a divisional of 09/221,540.

11.2. In the case of Serial No. 09/144,607, there is nothing in the prior art or the earlier application which shows that the inclusion of a rare earth component in the vanadium-containing catalytic materials would have been expected to have any desirable effect on the sulfur content of the liquid cracking products: rare earths have not been known to have any sulfur removal properties and their interactively synergistic effect here with the vanadium component, as shown in Table 4, indicates that the use of the rare earth in combination with the vanadium is patentably distinct from the use of vanadium alone. The double patenting rejection base on 09/144,607 should therefore be reconsidered.

12. In view of the amendments and remarks set out above, allowance of the application is requested.

27 August 2001
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Fluid Catalytic Cracking

Handbook

Reza Sadeghbeigi



Gulf Publishing Company

To my wife Connie
and our children Jessica and Jason
for their understanding and support.

Fluid Catalytic Cracking Handbook

Design, Operation, and Troubleshooting of FCC Facilities

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12. Scherzer, J. and McArthur, D. P., "Nitrogen Resistance of FCC Catalysts," presented at Katalistiks' 8th Annual FCC Symposium, Venice, Italy, 1986.
13. Dougan, T. J., Alkemade, V., Lakhampel, B., and Brock, L. T., "Advances in FCC Vanadium Tolerance," presented at NPRA Annual Meeting, San Antonio, Texas, March 20, 1994; reprinted in *Grace Davison Catalagran*.

CHAPTER 3

FCC Catalysts

The introduction of zeolite in commercial FCC catalysts in the early 1960s was one of the most significant advances in the history of FCC cracking. It provided the refiner a greater profit with little capital investment. Simply stated, zeolite cracking catalysts were and still are the biggest bargains of all time for the refiner. Continual improvements in catalyst technology have enabled refiners to continue to meet the demands of their market with minimum capital investment.

Compared to previous amorphous silica-alumina catalysts, the zeolite catalysts are more active and more selective. The higher activity and selectivity translate to more profitable liquid product yields and additional cracking capacity. In addition, to take full advantage of the zeolite catalysts, refiners have revamped older units to economically crack more of the heavier, lower-value feedstocks.

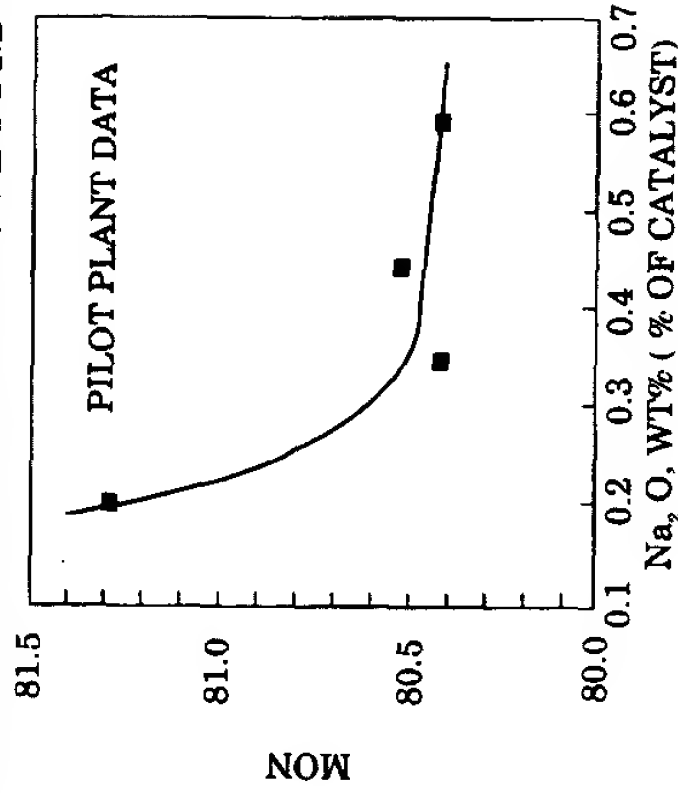
A complete discussion of FCC catalysts would fill another book. The intent of this chapter is to provide the information needed to select the proper catalyst and to troubleshoot the unit's operation. The key topics discussed are as follows:

- Catalyst Components
- Catalyst Manufacturing Techniques
- Fresh Catalyst Properties
- Equilibrium Catalyst Analysis
- Catalyst Management
- Catalyst Evaluation
- Additives

3.1 CATALYST COMPONENTS

FCC catalysts are in the form of fine powders with an average particle size diameter in the range of 75 microns. A modern cracking catalyst has four major component systems: zeolite, matrix, binder, and filler.

MOTOR OCTANE VS. SODIUM OXIDE



RESEARCH OCTANE VS. SODIUM OXIDE

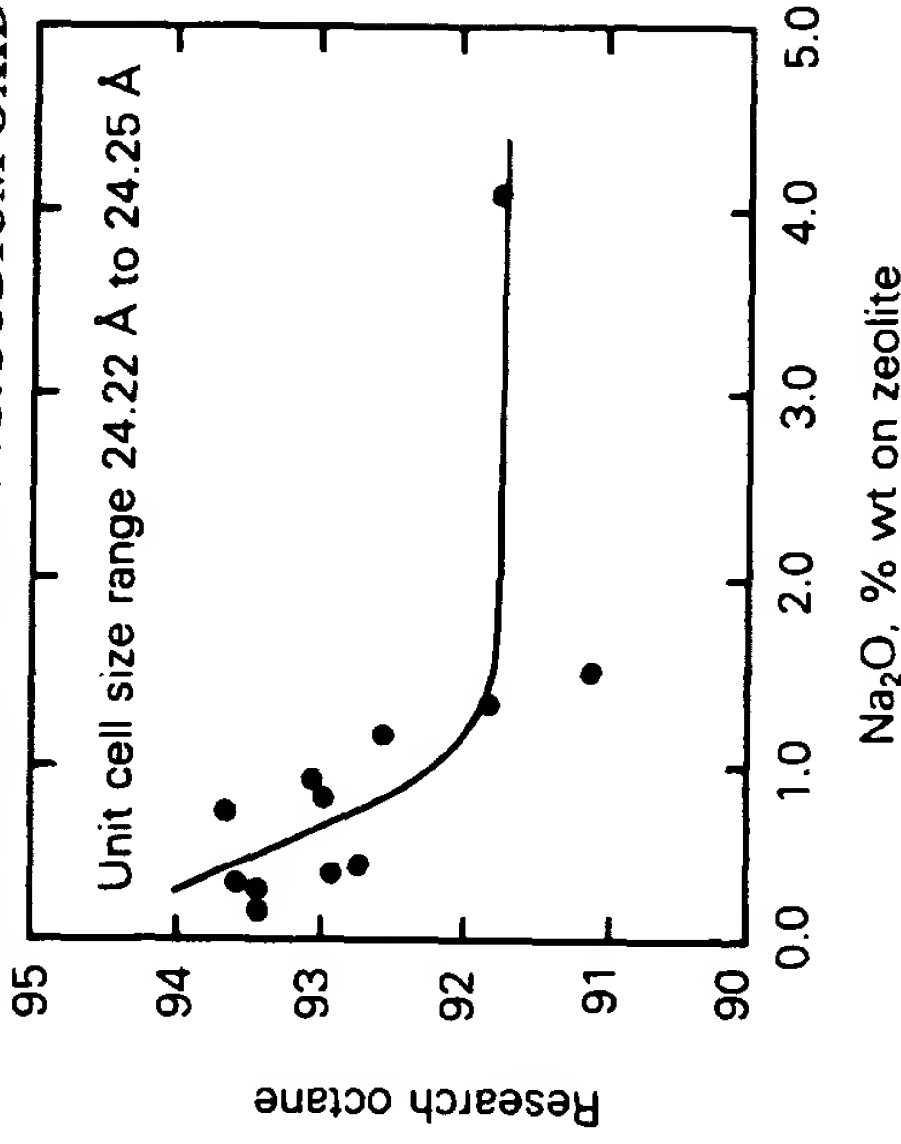


Figure 3-7. Effects of soda on motor and research octanes: motor octane vs. sodium oxide [11]; research octane vs. sodium oxide [4].

For others, matrix is a component of the catalyst aside from the zeolite having catalytic activity. Yet for others, matrix refers to the catalyst binder. In this chapter, matrix means components of the catalyst other than zeolite and the term *active matrix* means the component of the catalyst other than zeolite having catalytic activity.

Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure.

Active matrix contributes significantly to the overall performance of the FCC catalyst. The zeolite pores are not suitable for cracking of the large hydrocarbon molecules generally having an end point $>900^{\circ}\text{F}$; they are too small to allow diffusion of the large molecules to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst.

An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which the activity attained by their combined effects can be greater than the sum of their individual effects [2].

An active matrix can also serve as a trap to catch some of the vanadium and basic nitrogen. The high boiling fraction of the FCC feed usually contains metals and basic nitrogen that poison the zeolite. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated prematurely by these impurities.

3.1.3 Filler and Binder

The *filler* is a clay incorporated into the catalyst to dilute its activity. Kaoline [$\text{Al}_2(\text{OH})_2\text{Si}_2\text{O}_5$] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaoline clay as a skeleton to grow the zeolite in situ.

The *binder* serves as a glue to hold the zeolite, the matrix, and the filler together. Binder may or may not have catalytic activity. The importance of the binder becomes more prominent with catalysts that contain high concentrations of zeolite.

The functions of the filler and the binder are to provide physical integrity (density, attrition resistance, particle size distribution, etc.) a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

In summary, zeolite is the primary ingredient for selective cracking. Changes to the zeolite will affect activity, selectivity, and product quality. An active matrix can improve bottoms cracking and resist vanadium and nitrogen attacks. But a matrix containing very small pores can suppress strippability of the spent catalyst and increase hydrogen yield in the presence of nickel. Clay and binder provide physical integrity and mechanical strength.

(text continued from page 85)

Rare Earth Level. Rare earth elements serve as a "bridge" to stabilize aluminum atoms in the zeolite structure. They prevent the aluminum atoms from separating from the zeolite lattice when the catalyst is exposed to high-temperature steam in the regenerator.

A fully rare-earth-exchanged zeolite equilibrates at a high UCS, whereas a non-rare-earth zeolite equilibrates at a very low UCS in the range of 24.25 [3]. All intermediate levels of rare-earth-exchanged zeolite can be produced. The rare earth increases zeolite activity and gasoline selectivity with a loss in octane (Figure 3-6). The octane loss is due to promotion of hydrogen transfer reactions. The insertion of rare earth maintains more and closer acid sites, which promotes hydrogen transfer reactions. In addition, rare earth improves thermal and hydrothermal stability of the zeolite. To improve the activity of a USY zeolite, the catalyst suppliers frequently add some rare earth to the zeolite.

Sodium Content. The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain very low amounts of sodium.

Sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid sites to reduce the catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acid sites. In a dealuminated zeolite where the UCS is low (24.22 °A to 24.25 °A), the sodium can have an adverse affect on the gasoline octane (Figure 3-7). The loss of octane is attributed to the drop in the number of strong acid sites.

FCC catalyst vendors are now able to manufacture catalysts with a sodium content of less than 0.20 wt%. Sodium is commonly reported as the weight percent of sodium or soda (Na_2O) on the catalyst. The proper way to compare sodium is the weight fraction of sodium in the zeolite. This is because FCC catalysts have different zeolite concentrations.

UCS, rare earth, and sodium are just three of the parameters that are readily available to characterize the zeolite properties. They provide valuable information about catalyst behavior in the cat cracker. If required, additional tests can be conducted to examine other zeolite properties.

3.1.2 Matrix

The term *matrix* has different meanings to different people. For some, matrix refers to components of the catalyst other than the zeolite.

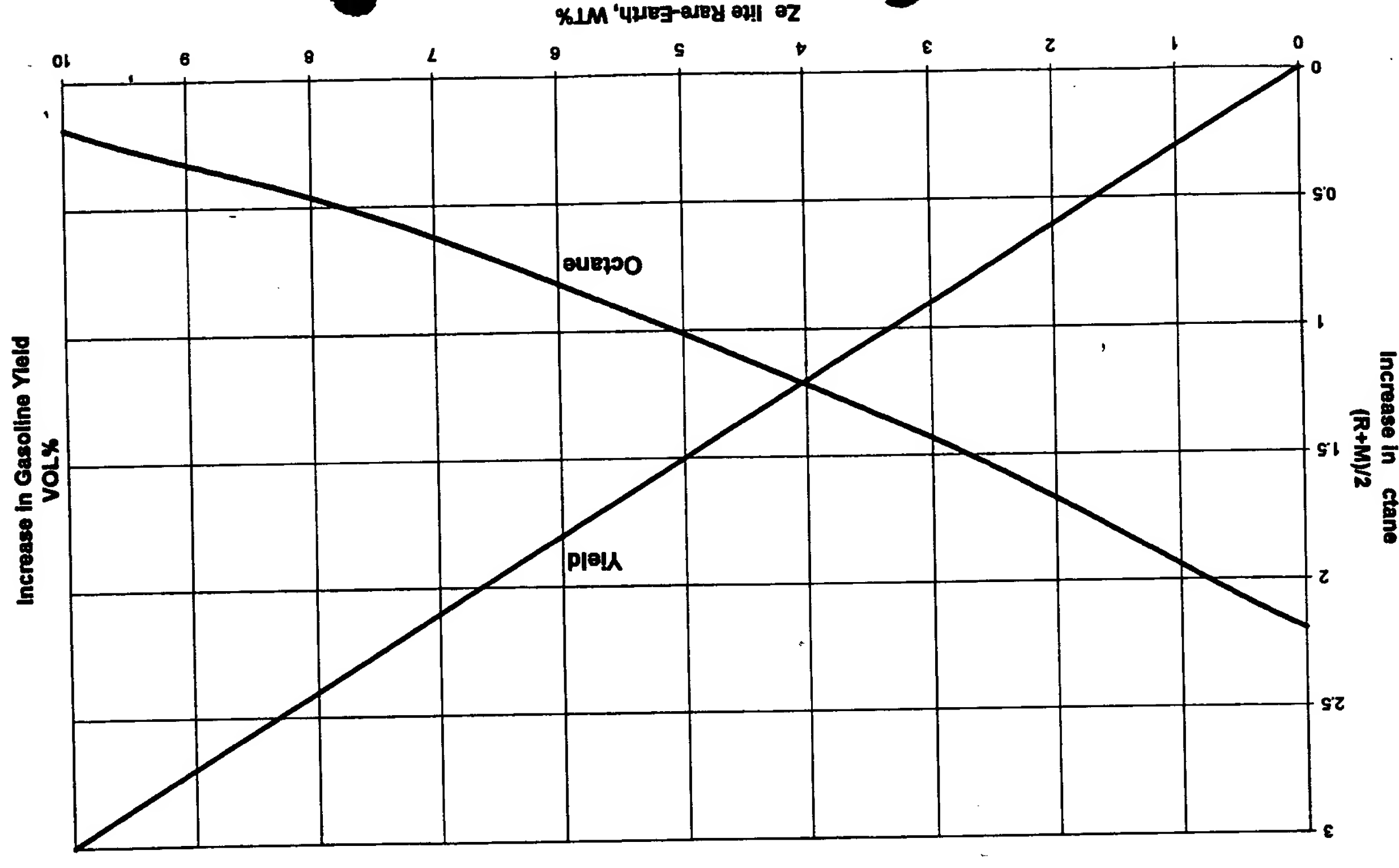


Figure 3-6. Effects of rare earth on gasoline octane and yield.